Algae Biomass Summit 2022

Mass transfer coefficients, k_L, and air-CO_2 ingassing rates in 3.4 m^2 and 1-acre raceway ponds

October 19, 2022

Braden Crowe (Presenting), Aubrey Davis, Erik Hoffnagle, Maria Reyna, Cooper Gibson, Ernesto Ortiz, John Benemann (P.I.)

Jakob Nalley, Eneko Ganuza, Bart Reid

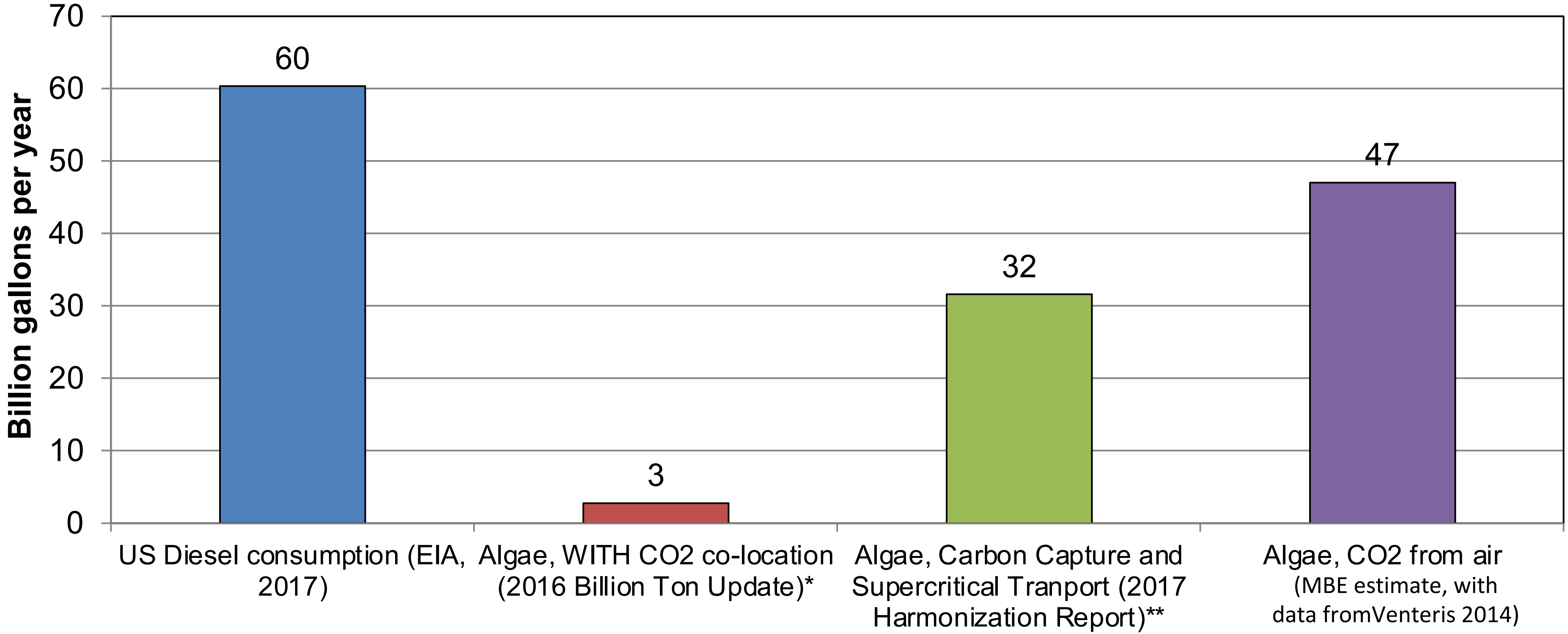
Michael Huesemann, Scott Edmundson, Song Gao

Dan Fishman (Project Officer)
Evan Mueller (Project Monitor)

DOE-BETO Award DE-EE008519

Why grow algae on CO_2 from air?

CO_2 point-source co-location limits algal resource potential to less than 5 BGY
Direct, in-pond air-CO_2 capture can increase resource potential nearly 10-fold



*freshwater and saltwater scenario, present productivity. Assume 0.35 g diesel/gas per g of biomass.

**Assume 0.35 g diesel/gas per g of biomass (for comparison to the 2016 BTU case)

The CO_2 mass-transfer rate, J_{CO_2}, is proportional to the mass transfer coefficient, k_L, and the 'driving force' for mass transfer. E accounts for chemical reactions.

$$J_{CO_2} [=] \frac{g\ C}{m^2-day} = k_L * \left(P_{CO2}^{air} * H - C_{CO2}^{bulk}(x = \delta)\right) * E$$

- k_L: Piston velocity
- $\left(P_{CO2}^{air} * H - C_{CO2}^{bulk}(x = \delta)\right)$: Driving force
- $C_{CO2}^{bulk}(x = \delta)$: Back pressure
- E: Enhancement factor (if reactions present)

When $C_{CO2}^{bulk}(x = \delta) > P_{CO2}^{air} * H$:

- Driving force is negative
- CO_2 lost from pond to atmosphere
- Net CO_2 'outgassing' rate

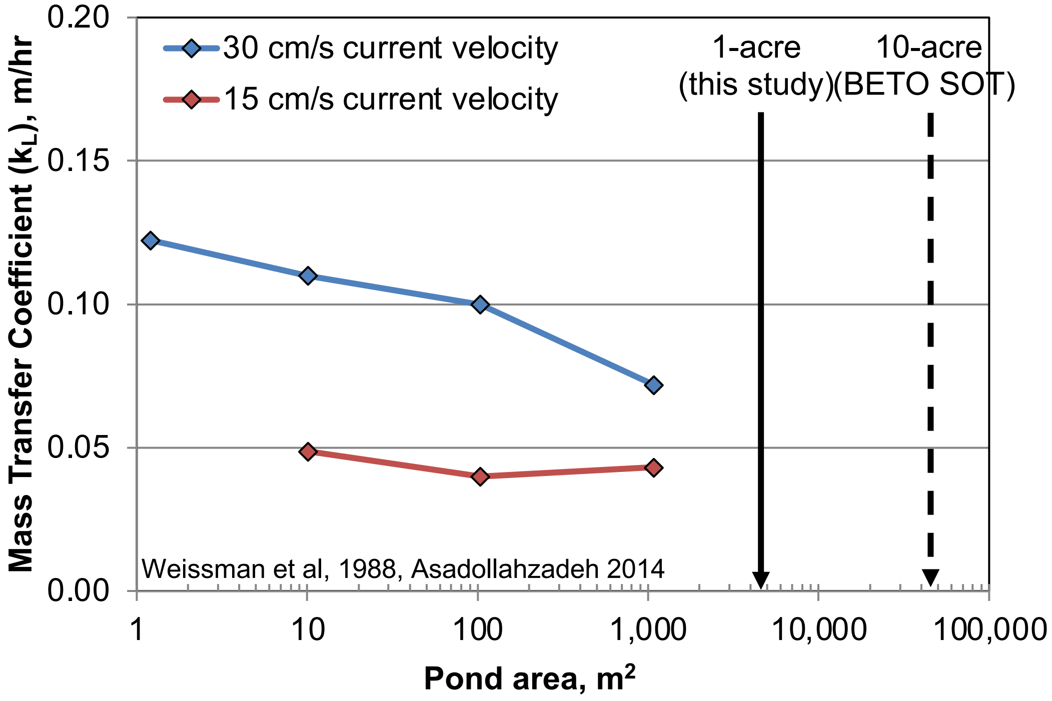
When $C_{CO2}^{bulk}(x = \delta) < P_{CO2}^{air} * H$

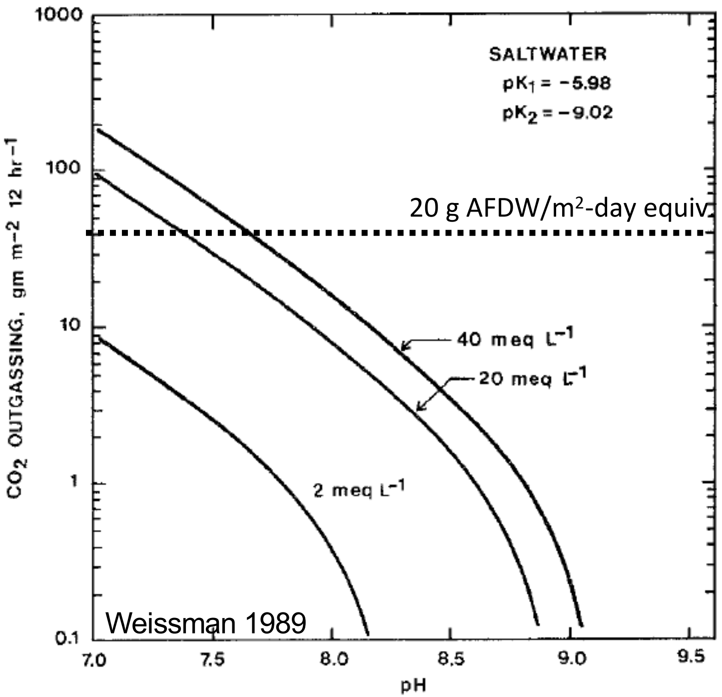
- Driving force is positive
- Air-CO_2 transfer from atmosphere to pond
- Net CO_2 'ingassing' rate
- Influence of reactions accounted with 'E'

Outgassing rates must be minimized to achieve high carbon utilization efficiency
Ingassing rates of are interest for direct algae air-CO_2 capture

k_L is between 0.05-0.1 m/hr for small ponds, unmeasured in large (1-acre +) ponds

At elevated alkalinity, pH 7.5 – 8.0, CO_2 outgassing rates approach the daily gain in biomass



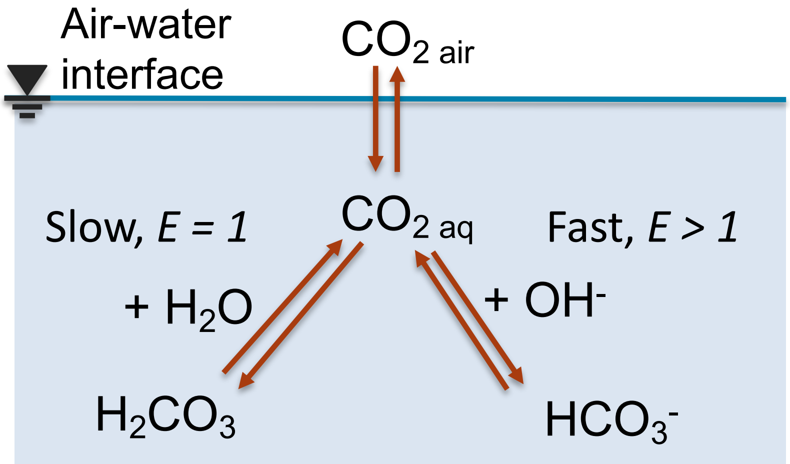


Influence of k_L, pond scale on the ingassing rate is uncertain, dependent on *E*

At elevated pH, the $CO_{2,aq}$ + OH^- reaction pathway appreciably increases air-CO_2 flux, known as chemical enhancement

Without chemical enhancement, $E = 1$, and air-CO_2 flux is given by:

$$J_{CO_2} = k_L * (C_{CO2}^{sat} - C_{CO2}^{bulk}) * E$$



Where:

C_{CO2}^{sat} = $CO_{2\,aq}$ at the air-water interface, in equilibrium with the gas phase, ~10 μM

C_{CO2}^{bulk} = $CO_{2\,aq}$ in pond 'bulk', ~0 μM at pH > 10

k_L= mass transfer coefficient, ~0.1 m/hr for ponds, a measure of turbulence as it relates to mass transfer

Under non-enhanced ($E = 1$) conditions:

$$J_{CO_2} = 0.1\,\frac{m}{hr}(10 - 0\,\mu M) = 0.3\,\frac{g\ C}{m^2 day} \approx 0.6\,\frac{g\ AFDW}{m^2 day}$$

E must be ~ 30 to support 20 g AFDW/m^2-day!

Depending on the assumed mass-transfer regime, estimates for E range from 2 to 40 at pH 10.5

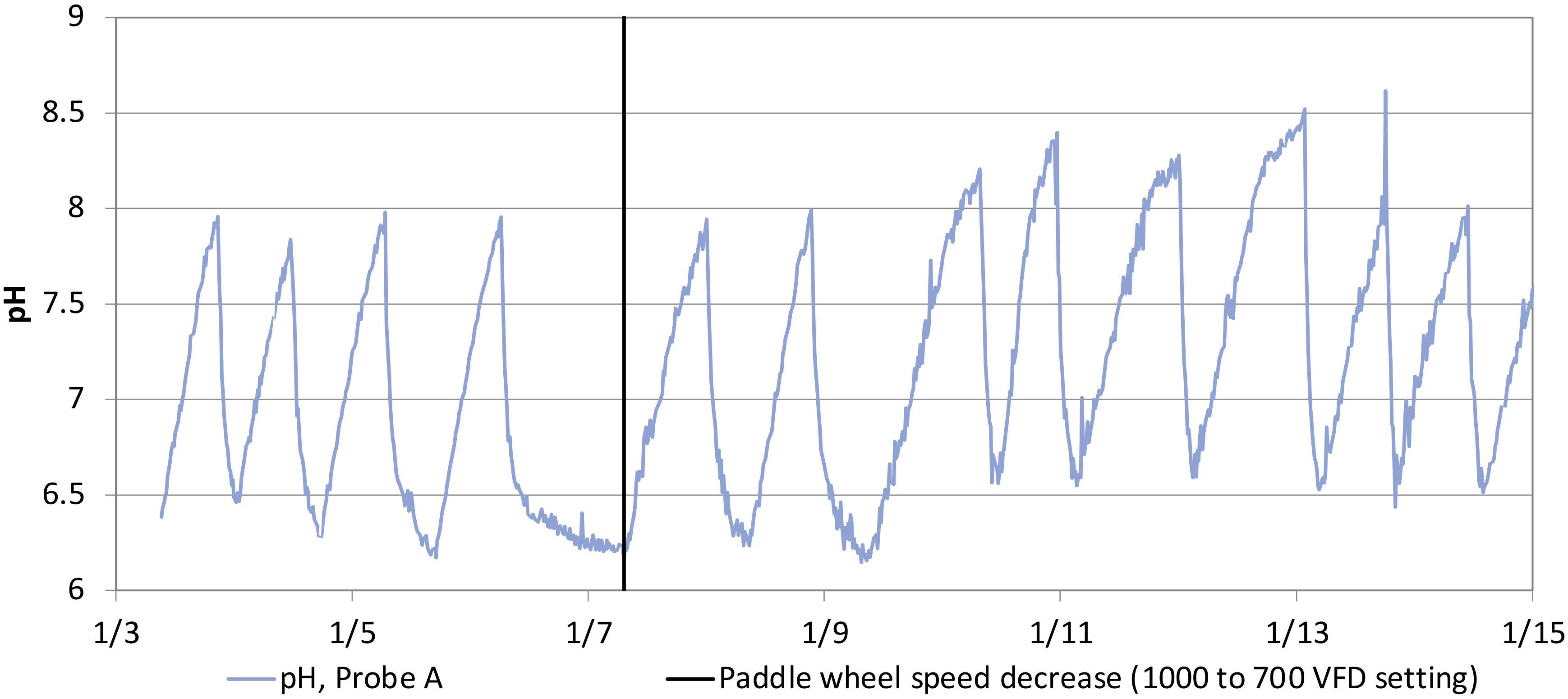
Hypothesis: *E is* sufficient to support high rates of carbon uptake, at a biologically compatible high pH

Approach – Identify conditions to meet the target air-CO_2 flux

- Measure air-CO_2 exchange rates via abiotic (without algae) trials in 1-acre ponds.
  - k_L is measured in 'outgassing trials', by supersaturating the pond with CO_2, then measuring the rate of pH increase.
  - Air-CO_2 flux, J_{CO_2}, at elevated pH is measured by displacing the pond from air-equilibrium with a strong base, then measuring the rate of return to equilibrium (pH decrease)
- Compare ingassing rates over a wider current velocity range in more easily managed 3.4 m^2 ponds
- Compare experimental results to model predictions to identify the appropriate mass-transfer model

Top: 1-acre ponds at QH, used to measure ingassing rates at a commercially relevant scale. Bottom: MBE 3.4 m^2 used to more fully parameterize air-CO_2 flux.

The mass transfer coefficient was measured at two paddle wheel speed settings over 13 cyles

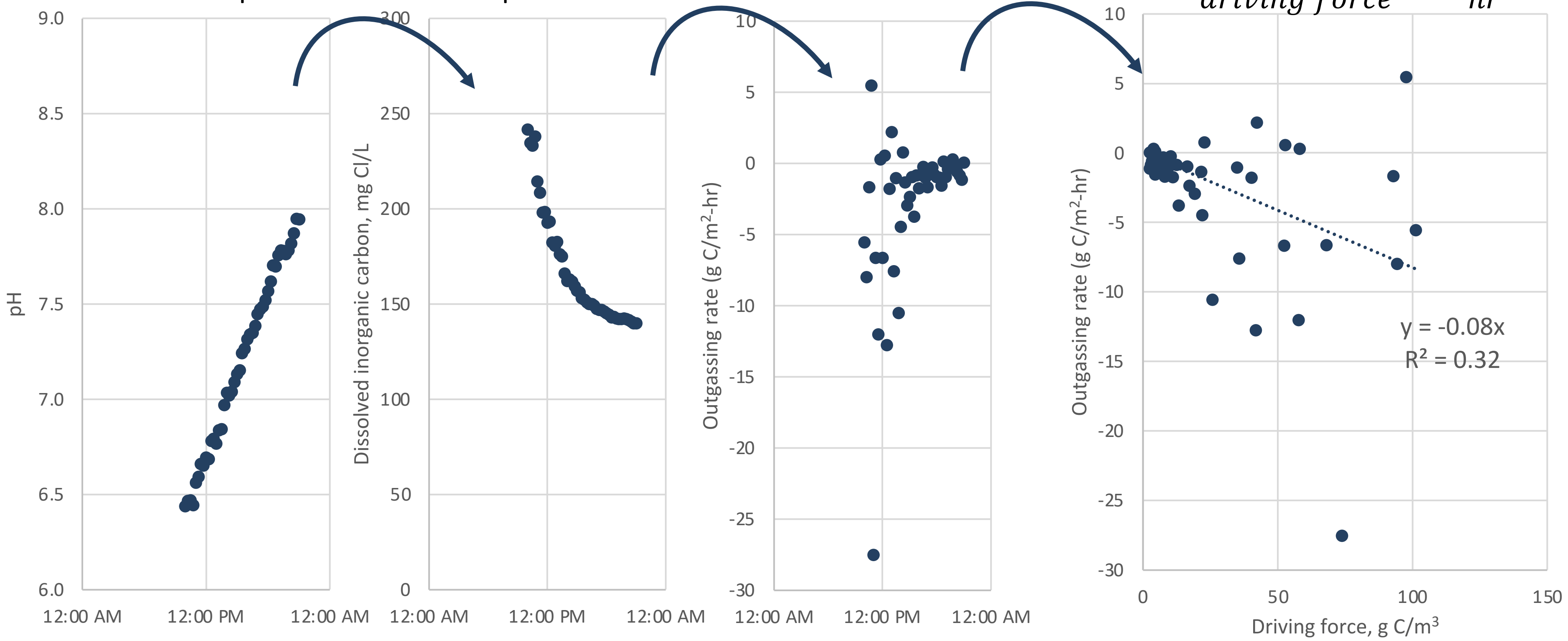


k_L is calculated from pH vs. time curves

Calculated from pH, alkalinity, equilibrium relationships

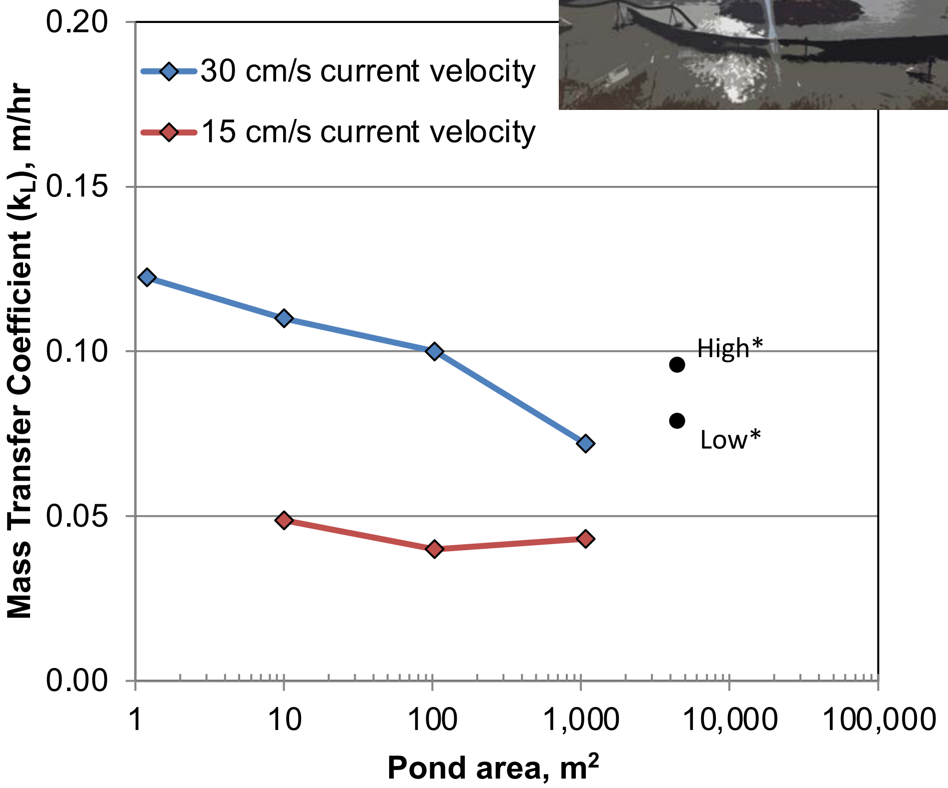
Outgassing rate = $\frac{\Delta IC}{\Delta time}$

$$k_L = \frac{Outgassing\ rate}{driving\ force} [=] \frac{m}{hr}$$



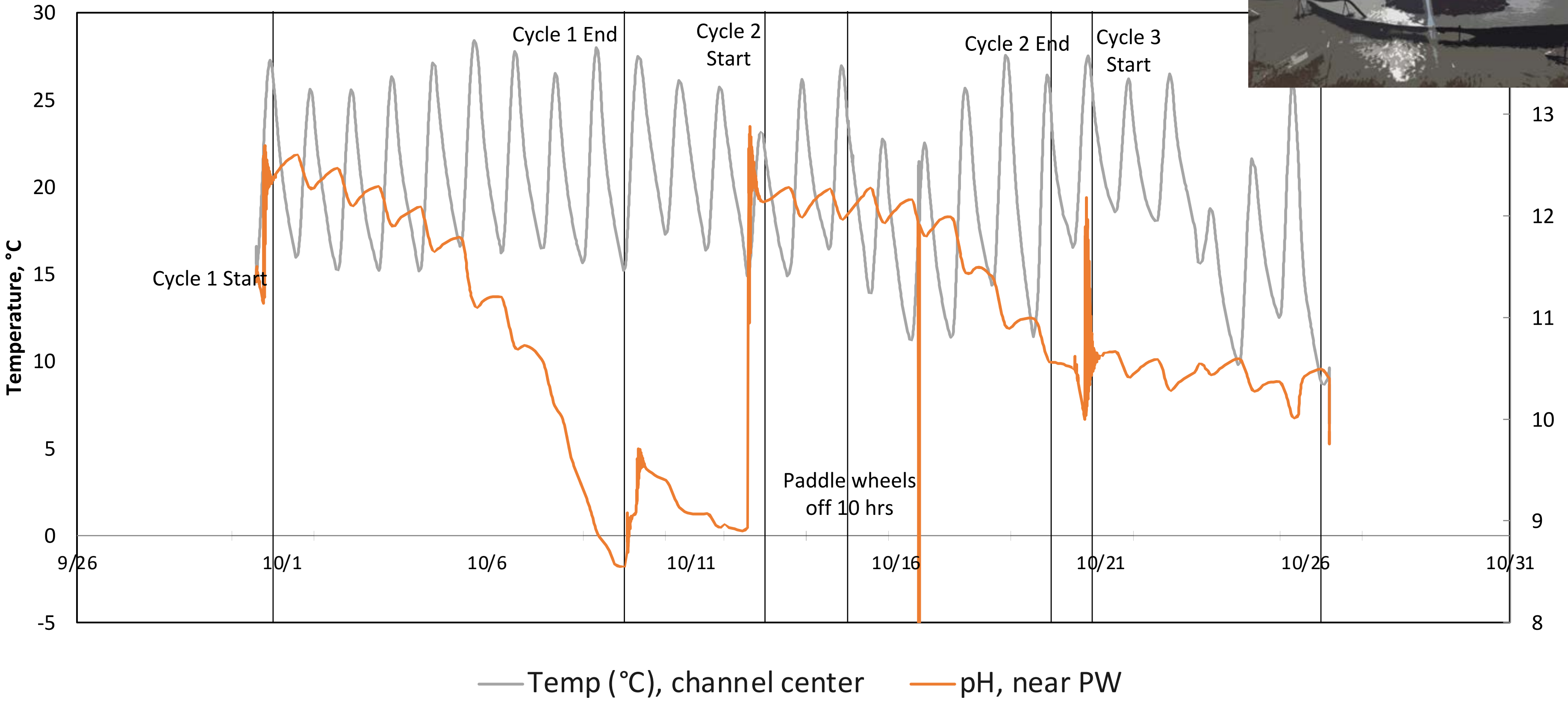
k_L measured 0.08 – 0.10, higher than hypothesized

Cycle #	High	Low
1	0.11	
2	0.08	
3	0.09	
4	0.11	
5		0.09
6		0.08
7		0.11
8		0.19*
9		0.07
10		0.07
11		0.09
12		0.08
13		0.07
AVG:	**0.10**	**0.08**
STDEV:	**0.01**	**0.01**
RSD:	**13.6%**	**16.3%**

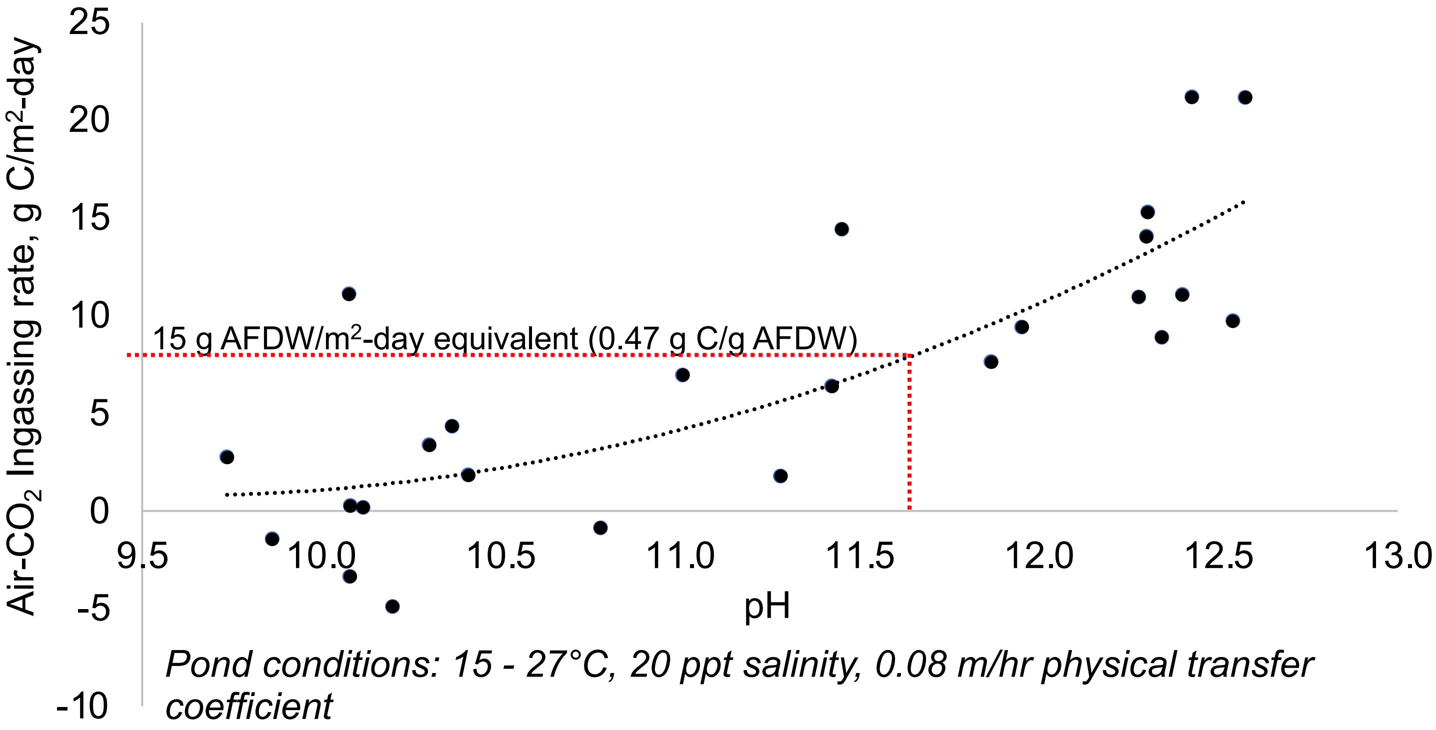


*Current velocity during 1-acre pond measurements TBD

Abiotic air-CO_2 ingassing rates were measured over three cycles, beginning above pH 12



1-acre pond ingassing rates rates increase with pH due to chemical enhancement; pH > 11.7 required to support 15 g AFDW/m²-day



<u>> pH 12 required to support 2025 DOE productivity target</u>

QUALITAS HEALTH

Mass-transfer model predictions of *E*, for two limiting cases:

Second order instantaneous reversible reaction, 'Diffusion Limited' (Olander 1960)

$$J_{CO_2} = k_L * \left(P_{CO2}^{air} * H - C_{CO2}^{*}(x=\delta)\right) * \left[1 + \frac{D_{OH^-}.D_{HCO_3^-}\cdot K\cdot[OH^-]}{D_{CO_2}\left(K\cdot CO_{2(aq)}^{*}\cdot D_{HCO_3^-} + D_{OH^-}\right)}\right]$$

$$K = \frac{[HCO_3^-]}{[OH^-][CO_2]}$$

Flux increases proportionally to turbulence

pH dependent, but not influenced by CO_2+OH^- reaction rate

First-order, finite reaction rate, 'Reaction Rate Limited' (Hatta 1932)

$$J_{CO_2} = \left(P_{CO2}^{air} * H - C_{CO2}^{*}(x=\delta)\right) * \left[\sqrt{\mathcal{D}_{CO2} * k_{tot} * [OH^-]} * \coth\left(\sqrt{\frac{\mathcal{D}_{CO2} * k_{tot}}{(k_L)^2}}\right)\right]$$

Square root reaction rate dependance

Turbulence independent when $\sqrt{\frac{\mathcal{D}_{CO2} * k_{tot}}{(k_L)^2}} < \sim 2$

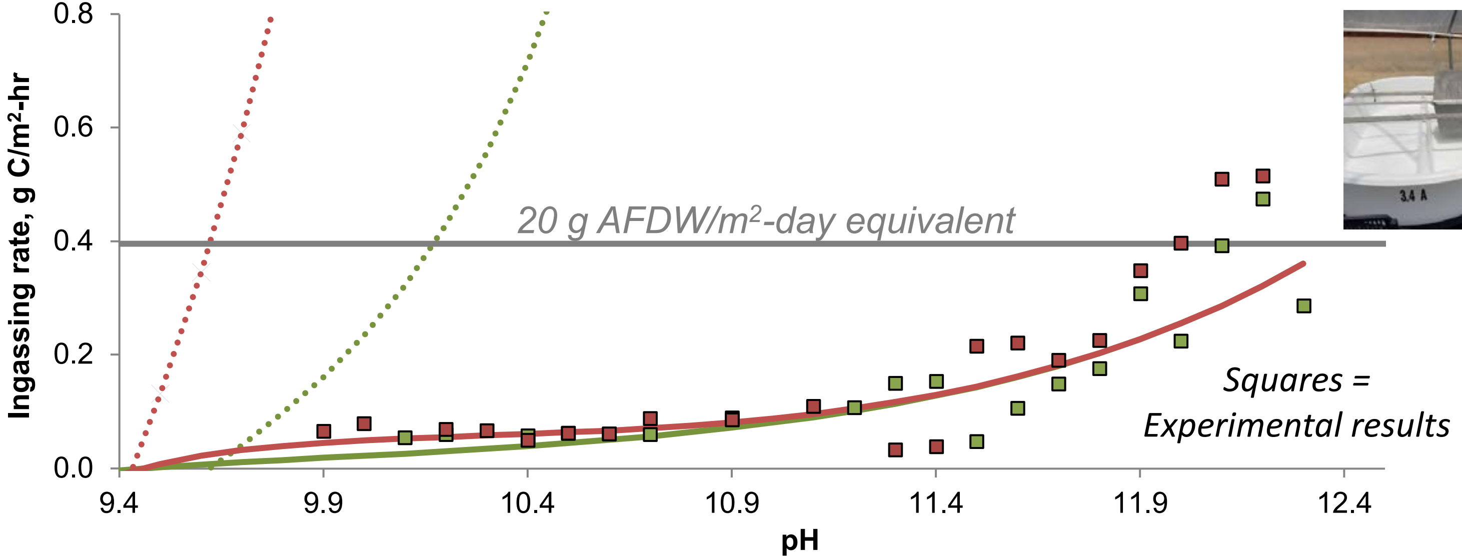
Transfer coefficient measurements repeated in 3.4 m^2 ponds, aiming to find paddle wheel setting, depth yielding ‘fast’ and ‘slow’ k_L in follow-on ingassing trial

Paddlewheel VFD setting (Hz)	Pond	Depth (cm)	k_L (m/hr)	kl Error	n
45	A	30	0.22	0.01	84
45	A	25	0.29	0.01	76
45	**B**	**30**	**0.36**	**0.02**	**209**
35	A	25	0.20	0.01	485
30	A	30	0.12	0.01	83
30	B	30	0.22	0.01	83
20	**A**	**30**	**0.06**	**0.01**	**26**
20	B	30	0.07	0.01	26
15	A	30	0.04	0.01	7
15	B	30	0.05	0.01	7
10	A	30	0.03	0.01	13
10	B	30	0.03	0.01	13

$$k_L = \frac{Outgassing\ rate}{driving\ force} [=] \frac{m}{hr}$$

Experimental data validates the reaction-rate limited model; air-CO_2 flux is independent of the mass-transfer coefficient, k_L

Model predictions for 'diffusion' (dotted lines) and 'reaction rate' limited (solid lines) transfer, at low (kL = 0.06 m/hr) and high (kL = 0.36 m/hr) turbulence levels



Conclusion: Decreases in turbulence levels in 10-acre ponds are not expected to influence chemically enhanced air-CO_2 flux.

Conclusions

- Chemically enhanced air-CO_2 absorption requires high pH, 12 or above, to support economically viable biomass productivity
- Finding strains that thrive at such a high pH will be a challenge
- Experimentally measured ingassing rates align well with the ‘reaction-rate limited’ mass-transfer regime; ingassing rates appear minimally influenced by pond scale

Thank you!

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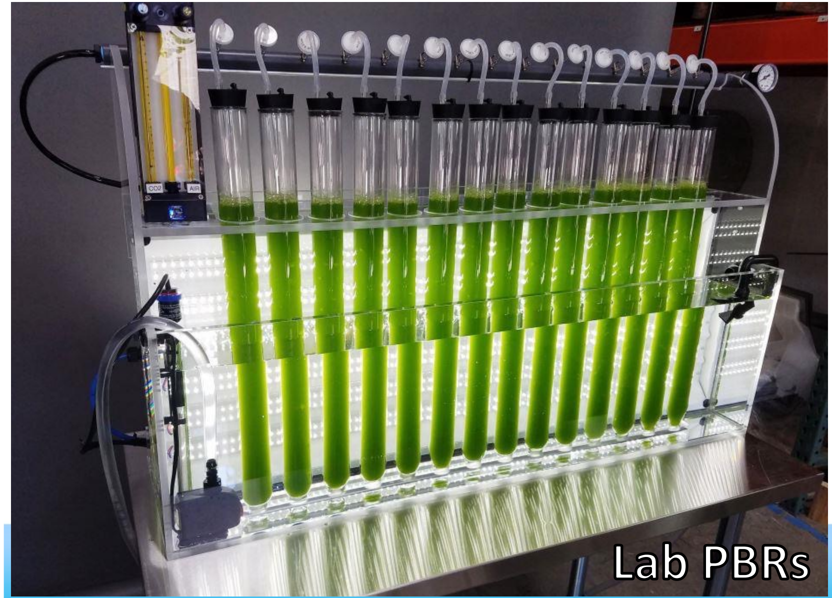

Acknowledgment

This work is supported by the U.S Department of Energy (DOE):
Bioenergy Technologies Office (BETO).

"AIR CARBON FOR ALGAE PRODUCTION - AIRCAP.", DE-EE0008519, 2018-2022.

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